AD-A067 599 HARVARD UNIV CAMBRIDGE MA DIV OF APPLIED SCIENCES F/G 20/12

IMPURITY EFFECTS IN AMORPHOUS SEMICONDUCTORS.(U)

MAR 79 W PAUL DAAG29-77-G-0059

UNCLASSIFIED ARO-14454.1-P NL

| OF |

AD A067599

END

DATE FILMED

6-79

DDC

11 18 ARO 19 14454.1-P

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Final Report I	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 IMPURITY EFFECTS IN AMORPHOUS SEMICONDUCTORS.		5. TYPE OF REPORT & PERIOD COVERED Final Report 1/1/77-12/31/78
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 William/Paul		8. CONTRACT OR GRANT NUMBER(s) 15 DAAG29-77G-0059, NSF-DMR76-01111
9. PERFORMING ORGANIZATION NAME AND ADDRESS Division of Applied Sciences, Harvard University Cambridge, MA. 02138 12 19p.		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 11 1 March 1979
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) 9 Rept. no. 1 (Final), 1 Jan 77-31 Dec 78, LEVEL II		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Amorphous semiconductors
Amorphous silicon devices

GREATER THAN

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This research is directed toward the discovery of the preparation conditions and material properties which will yield amorphous silicon-hydrogen alloys with the lowest density of defect-related states in the energy gap and/or the best photo-response. Among the effects investigated were the results of varying the substrate temperature and the partial pressures of hydrogen, argon and oxygen in the sputter-gas mixture. It was established that too high a substrate temperature (say, >300°C) led to the incorporation of less hydrogen and to a larger gap state density. It was also established that films containing the same concentration of

over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified LB

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

410 457

20. Abstract continued

hydrogen, but prepared under different conditions of hydrogen partial pressure, showed different behavior as regards transport, photo transport, photoluminescence and absorption. These data were explained in terms of different state densities in the energy gap. Variation of the argon partial pressure was shown to give films of different conductivity and photoconductivity, and an argument was made that there was an optimum argon pressure: the critical argon pressure corresponded to that which was sufficient to reduce the mean free path of the sputtered silicon below the interelectrode separation.

79 04 16 060

IMPURITY EFFECTS IN AMORPHOUS SEMICONDUCTORS

FINAL REPORT I

WILLIAM PAUL

1 MARCH 1979

U. S. ARMY RESEARCH OFFICE

GRANT DAAG2977G0059

HARVARD UNIVERSITY
CAMBRIDGE, MASS. 02138

INTRODUCTION

This report concerns an investigation into the general effects of hydrogen incorporation into amorphous silicon with a specific thrust toward the reduction of the density of defect related states in the pseudogap and a resultant improvement in the photoconductive response.

CONTENTS

REPORT

Introduction

Prior to this Research Agreement, research at this laboratory had shown that, when amorphous Si was produced by rf sputtering, the samples contained a large number of voids giving rise to unreconstructed dangling bonds. These defects produced electronic states in the gap between the valence and conduction bands which dominated the optical and transport properties of the material. When H_2 was added to the Ar sputtering gas, the majority of these dangling bonds were compensated by H and the density of gap states reduced by orders of magnitude. Subsequent addition of partial pressures of PH_3 or B_2H_6 led to the incorporation of "hydrogenic" dopants P or B, the Fermi level was moved toward the conduction or valence band edge and the material displayed dominant n or p type conduction by thermopower measurement. Sequential preparation of a-Si in plasmas of $(Ar + H_2 + PH_3)$ and $(Ar + H_2 + B_2H_6)$ were then used to produce n-p junctions. At first glance the best conditions for easy doping with P or B appeared to be the highest substrate temperature T_s which did not lead to crystallization and the highest H partial pressure p_H. When early experiments indicated that this was not the case, we embarked on a systematic examination of the effects on the optical absorption, the spin resonance, the electrical conductivity and the photoconductivity of varying T_s and p_H. The results indicated that there was an optimum T_s, above which H was not efficiently incorporated, and that many of the measured properties were nonlinear as a function of p_H. An abstract of a paper accepted for the 1977 Edinburgh Conference on Amorphous Semiconductors, which detailed these findings, is given in Appendix 3.

Subsequent work has elaborated on the search for the optimum conditions for sample preparation. A common thread in all of these separate investigations has been the mounting evidence that certain conditions of preparation lead to H-incorporation in a fashion which maintains or catalyzes electronic energy levels in the semiconductor pseudo-gap.

Effect of Varying Substrate Temperature T_s

Above $T_s = 200$ to 250°C the H is not efficiently incorporated. This has been verified in four separate experiments

(1) hydrogen is evolved on heating the sample above 200-250°C.

(2) the integrated optical absorption at the frequency for Si-H stretching modes decreases at fixed hydrogen partial pressure p_H, for $T_s > 200$-250°C. This is reported in the article by Freeman and Paul, abstract in Appendix 3.

(3) the shift of the absorption edge with increasing T_s at fixed p_H reverses above 250°C, as a result of reduced H-incorporation which decreases the gap state density. See Freeman and Paul, Appendix 3.

(4) the transport changes from an activated type to high magnitude, hopping conductivity through states in the gap as T_s is raised above 250°C.

It therefore appears to be clear that less H is incorporated at higher T_s. Undecided by these measurements is the question whether a very high T_s, accompanied by a very high H partial pressure p_H, might still lead to the lowest gap state density. It is conceivable that the healing effect of high T_s might be beneficial and that high p_H would still result in adequate H-incorporation to mop up residual defects.

Effect of Varying H Partial Pressure p_H at Fixed T_s

It has been established that, at fixed T_s, the properties depend on the value of p_H as well as the hydrogen incorporation C_H. The evidence may be summarized as follows

(1) the fine structure in the vibrational absorption due to Si-H complexes is not simply dependent on C_H, but on p_H also.

(2) the optical absorption edge, and the deduced optical energy gap, is a double-valued function of C_H. The details are discussed in Freeman and Paul, Appendix 3. The tentative conclusion is that increasing p_H may lead to a higher density of states in the energy gap.

(3) field effect measurements indicate that material prepared at high p_H has a higher density of states in the gap than material of the same C_H prepared at lower p_H.

(4) the photoluminuescence is decreased in material prepared at fixed C_H, but high p_H, and a strong feature appears at 0.8 eV to modify the spectral dependence.

(5) the photoconductivity is <u>increased</u> in the material made at high p_H, which has a higher gap state density.

(6) structure appears in the photoconductivity spectrum for the high p_H material.

All of these data are self-consistently explained by the postulate that, in material prepared at high p_H, there exist states in the gap that are absent in material prepared at lower p_H that has nevertheless the same H-content.

<u>Effect of Varying the Argon Sputtering Pressure</u>

The reason for investigating the possible effect of varying the argon sputtering pressure is the likelihood of bombardment of the film during growth, either by high energy A atoms and ions or by silicon atoms which have not been completely thermalized before striking the substrate. The effect of such bombardment is to <u>create</u> defects in the film which the H cannot compensate. It can (in principle) be eliminated by increasing the argon sputtering pressure, which reduces the mean free path of all species in the plasma.

Our results indicate that this is exactly what happens. Films prepared at higher argon pressure (10-30 mTorr compared with 5 mTorr in earlier work) have a higher photoconductivity and an improved photoluminescence efficiency. Additional significant changes have been observed in the temperature dependence of conductivity. Whereas in the earlier work the Fermi level always lay close to mid-gap, in the recent films the Fermi level appears to be pinned at an energy much closer to the conduction band. This result is of considerable importance in making a metal-semiconductor device, since for a fixed barrier height between metal and semiconductor, the diffusion potential (or equivalently the field inside the semiconductor) will be larger the closer the Fermi level is to the conduction band. Thus, photocarriers will be more rapidly swept out of the space charge region leading to a higher carrier collection efficiency.

This work will be published in the J. Vac. Science and Technology in June 1979. The reader is referred to Appendix 3 for an abstract.

Effect of Varying the Content of Oxygen

At the time of writing, the device performance of a-Si material prepared by sputtering is inferior to that of material prepared by glow discharge decomposition of SiH_4. We noted that the chemical purity of the materials and apparatus used in the glow discharge process was very likely inferior to that for the sputtering method, and that it was therefore worth investigating whether impurities played a beneficial role in a-Si-H. The most likely impurity appeared to be oxygen and so a quite extensive investigation of the dark transport, photoconductivity, photoluminescence and optical absorption of sputtered oxygenated Si-H alloys was carried out. The results indicated that O almost certainly played some role in these phenomena, but that the role was complex, and required further work. An abstract of a Physical Review Letter on this subject is given in Appendix 3.

Device Aspects

As our material was improved by increased understanding of the effects of varying T_s, p_H, P_{Ar} and P_O, we made new devices in Schottky configurations, and measured the properties. Our progress on this front was reported in Progress Report No. 2, covering the period up to December 31, 1977. Although the work on oxygen incorporation and argon pressure change was subsequent to that period there was not sufficient time left when this Research Agreement terminated to exploit the very significant advances the basic work foreshadowed.

APPENDIX 1: Personnel

Professor William Paul,	Principal Investigator
Dr. David A. Anderson,	Research Fellow
Ms. Eva Freeman,	Research Assistant
Mr. J.R. Pawlik,	Research Assistant

APPENDIX 2: Publication List

1. Effect of hydrogen on the transport properties of amorphous silicon. D.A. Anderson, T.D. Moustakas and William Paul, Proceedings of the 7th International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977, p. 334.

2. Transport in doped sputtered a-Si-H. D.A. Anderson, Bull. Am. Phys. Soc., March, 1978.

3. Optical constants of r.f. sputtered hydrogenated amorphous Si. E.C. Freeman and William Paul, submitted for publication in the Physical Review.

4. New development in the study of amorphous silicon hydrogen alloys: The story of O. M.A. Paesler, D.A. Anderson, E.C. Freeman, G. Moddel and William Paul, Phys. Rev. Lett., 41, 1492 (1978).

5. The importance of argon pressure in the preparation of r.f. sputtered amorphous Si-H alloys. D.A. Anderson, G. Moddel, M.A. Paesler and William Paul, accepted for publication in J. Vac. Science and Technology.

6. Phototransport and its time decay in r.f. sputtered a-Si-H. G. Moddel and D.A. Anderson, Bull. Am. Phys. Soc., March, 1979.

EFFECT OF HYDROGEN ON THE TRANSPORT PROPERTIES OF AMORPHOUS SILICON*

By D.A. Anderson, T.D. Moustakas and W. Paul
Division of Applied Sciences, Harvard University
Cambridge, Massachusetts 02138 U.S.A.

Abstract

The influence of hydrogen on the transport properties of amorphous silicon has been investigated in a matrix of samples prepared at five temperatures T_s between 200 and 540°C and seven partial pressures p_H of hydrogen or deuterium. For $T_s \leq 350$°C, small amounts of hydrogen decrease the room temperature conductivity by up to seven orders of magnitude and reveal activated conduction between about 80 and 250°C. The activation energy first increases with p_H to a maximum of 0.9 eV and then decreases slightly. For $T_s > 350$°C, there are much weaker effects, which are attributed to less efficient hydrogen incorporation. The slope of thermopower vs 1/T is ≈ 0.15 eV smaller than the conductivity activation energy. The results are discussed in terms of the compensation of dangling bonds by the hydrogen and the possibility that large amounts of incorporated hydrogen influence the transport mechanism in the conduction band.

* Work supported by the National Science Foundation under Grant No. NSF-DMR76-15325, and by the U.S. Army under Grant No. DAAG29-77-G-0059

Abstract Submitted

for the Washington, D.C., Meeting of the

American Physical Society

27-30 March 1978

Physics and Astronomy
Classification Scheme
Number 72.80 Ng

Suggested title of session
in which paper should be placed
Amorphous Semiconductors

Transport in Doped Sputtered a-Si:H.* D.A. ANDERSON, Harvard U.**--We present measurements of conductivity and thermopower in a-Si:H films doped n or p-type by the addition of PH_3 or B_2H_6, respectively, to the sputtering gas. On the basis of our earlier investigation of undoped Si, a substrate temperature of 250°C and a partial pressure of hydrogen of 4×10^{-4} Torr were chosen as the optimum conditions for minimum gap state density. The presence of as little as 10^{-5} Torr PH_3 in the sputtering gas decreases the conductivity activation energy from approximately 0.75 eV to 0.25 eV as the Fermi level shifts towards the conduction band. The same pressure of B_2H_6 gives E_σ = 0.4 eV and conduction by holes. High accuracy thermopower measurements reveal structure in the temperature dependence which will be analysed in terms of possible transport in a donor band.

*Submitted by WILLIAM PAUL

**Supported by US Army Contract No. DAAG-29-77-G-0059.

Prefer Standard Session

William Paul

William Paul
Division of Applied Sciences
Harvard University, Pierce Hall
Cambridge, MA 02138

Optical Constants of r.f. Sputtered Hydrogenated Amorphous Si

E. C. Freeman and William Paul

Abstract

The transmission spectra of a-$Si_{1-x}H_x$ alloys prepared under different conditions of substrate temperature T_s and hydrogen partial pressure p_H have been measured over the region of the spectrum encompassing the absorption edge. The dependence of the refractive index on T_s and p_H and the photon energy has been established. The displacement of the absorption edge with T_s and p_H has been studied and related to the hydrogen content of the films and the detailed parameters of deposition. Changes in the absorption edge spectrum resulting from annealing have been correlated with the evolution of hydrogen. The addition of P and B dopants produces absorption at photon energies below the edge for the undoped material. Finally, the temperature dependence of the absorption edge between 4 and 300 K has been measured and compared with corresponding data for the crystal.

NEW DEVELOPMENT IN THE STUDY OF AMORPHOUS SILICON HYDROGEN ALLOYS: THE STORY OF O*

M.A. Paesler, D.A. Anderson, E.C. Freeman,
G. Moddel, and William Paul

Division of Applied Sciences
Harvard University, Cambridge, Massachusetts 02138

Abstract

We present results of dark-conductivity, photoconductivity, photoluminescence, and optical-absorption experiments on films of sputtered oxygenated amorphous-silicon-hydrogen alloys (a-$Si_{1-x}H_x$). Films with oxygen (O) are shown to behave much more like glow-discharge-produced a-$Si_{1-x}H_x$ than do O-free films. O is found to enter the amorphous matrix predominantly in an Si-O-Si bridging configuration. Defects associated with the presence of H are shown to be likely centers for radiative recombination, while both O and H may be associated with locally deformable defects.

*Work supported by the U.S. Army, Contract No. DAAG29-77-G-0059, the Joint Services, Contract No. N00014-75-C-0648, and the National Science Foundation, Contract No. DMR76-15325.

The Importance of Argon Pressure in the Preparation of r.f. Sputtered Amorphous Silicon-Hydorgen Alloys*

D.A. Anderson, G. Moddel, M.A. Paesler, and William Paul

Division of Applied Sciences
Harvard University, Cambridge, Massachusetts 02138

Abstract

We report the influence of argon partial pressure p_{Ar} on the photoconductivity, four-probe conductivity and photoluminescence of r.f. sputtered a-Si:H alloys. As p_{Ar} is increased from 5 to 30 mTorr, for fixed hydrogen partial pressure p_H, photoconductivity increases by as much as three orders of magnitude and then saturates. Over this range luminescence intensity increases, dark conductivity activation energy decreases and a plot of log conductivity versus inverse temperature becomes increasingly less linear. We note that high p_{Ar} films become slowly contaminated upon exposure to air. These results are interpreted in terms of a reduction in energetic silicon atom bombardment of the growing film with increased p_{Ar}. For our sputtering arrangement, we show that silicon atoms ejected from the target become significantly more thermalized at $p_{Ar} = 10$ mTorr than at 5 mTorr. Based primarily on the fact that the conductivity activation energy is more strongly dependent on p_H for low p_{Ar} films, we develop a model which suggests that higher argon pressures reduce damage-related deep gap states exposing low density structure in the electronic density of states.

*Work supported by the U.S. Army Research Office, Contract Number DAAG29-77-G-0059, and the National Science Foundation, Contract Number NSF-DMR76-01111.

Abstract Submitted
for the Chicago Meeting of the
American Physical Society
19-23 March 1979

Physics and Astronomy
Classification Scheme
Number 73.60 Fw
72.40 +w
72.20 Jv

Suggested title of session
in which paper should be placed
Hydrogenated Amorphous Silicon

Phototransport and Its Time Decay in rf Sputtered a-Si-H.* G. MODDEL and D.A. ANDERSON, Harvard U.**--We report photoconductive properties and related quantities of a-Si-H rf sputtered under different preparation conditions. Included are measurements of time decay, spectral response and temperature dependence as a function of illumination intensity. From photoconductivity magnitude and decay time ($\tau \sim 10^{-5}$ to 10^{-3} s) the room temperature drift mobility is calculated to be between 10^{-2} and 10^{-3} cm^2 V^{-1} s^{-1}. From the significant variations of decay time with light intensity, we suggest a model for carrier recombination. It is evident that evaluation of properties relevant to solar cell applications must be made under the appropriate illumination.

*Submitted by WILLIAM PAUL
**Supported by US Army Contract No. DAAG29-77-G-0059

Prefer Standard Session

William Paul

William Paul
Division of Applied Sciences
Harvard University, Pierce Hall
Cambridge, MA 02138